

## CHAPTER 2

### 2. RECENT ADVANCES IN CRYSTAL STRUCTURE SIMULATION AND UREA/THIOUREA STRUCTURE

In this Chapter we will review the methods presently applied to simulate crystal structure at empirical and *ab initio* levels. We will also consider the relevant data available at present in the literature on the structures and energies of molecular and crystalline urea and thiourea.

#### 2.1 Empirical force-field potentials

The first simulations of molecular crystals were done by means of analog modeling: molecules were represented as a collection of overlapping atomic solid spheres.<sup>1</sup> Digital extension of this model is called force-field and employs smooth potentials with simple analytical expressions, including number of empirically adjusted parameters. The most widely used form of nonbonded potential is the Buckingham potential (1-6-exp):

$$V(r_{ij}) = A \exp(B r_{ij}) - \frac{C}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}$$

where *i* and *j* are force centers of the different molecules. The repulsion exponent term is sometimes replaced with softer  $r_{ij}^{-12}$  or  $r_{ij}^{-10}$  dependence. The last term of this

expression is the Coulomb interaction of two point charges. The form of this function is justified by intermolecular perturbation theory (IMPT).<sup>2</sup> If one ignores overlap between molecular wavefunctions and treats the influence of the second molecule as a perturbation, an electrostatic term appears in the first order, while the dispersion  $r_{ij}^{-6}$  term appears in the second order along with polarization, which will be discussed below. To obtain the repulsion term one has to include overlap. This brings exchange repulsion in the first order, and cross-terms in the second order. The part of polarization term containing electronic excitations from occupied orbitals of one molecule into vacant orbitals of another is often regarded as charge transfer term. The resulting expression for energy becomes more complex, but at present, it is well-studied and coded in computer programs such as SAPT<sup>3</sup> and CADPAC.<sup>4</sup>

At early stages of force-field development, force centers were associated with atoms and parameters  $A$ ,  $B$ , and  $C$ , as well as the charges were adjusted to fit empirical data. Later the charges were obtained from population analysis of molecular wavefunction (for instance, by Mulliken) or by fitting the molecular electrostatic potential. At present there are several techniques applied for this purpose. Different in details, they all based on the set of point charges (PC) and multipoles distributed in space (not necessary on atoms). The values for these charges (multipoles) are obtained directly from the wave function with a projection technique or indirectly via a procedure of fitting values to the molecular electrostatic potential in the region of interest (usually in the range from 1 to 2 Van der Waals distances from any atom). We will compare these schemes in Chapter 6.

Additive transferable force-fields are the most computationally efficient representation of molecular electronic structure, and for this reason they are widely used for simulation of the structure and properties of condensed matter. However, they are not the most accurate and reliable way to describe molecular interactions. The necessity to develop models with polarizable potentials is clearly understood.<sup>5,6</sup> The traditional way to improve the force field method is to add polarizable centers to the model. Each of these centers is characterized by polarizability tensor  $\alpha$ , proportionality constant between the external electric field  $F$  and the induced dipole moment  $\mu$ :

$$\mu = \alpha F$$

Polarization allows the interaction energy to be a nonlinear function of the field strength. Dipolar (or second) polarizability is the derivative of the energy with respect to the field strength. The derivatives of the energy with respect to the field gradient (quadrupole polarizability, hyperpolarizability) makes description even more precise, but they are usually neglected for practical purposes.<sup>7</sup> The potential function has to be modified so that it includes the interaction of these induced dipole moments with point charges and with other dipole moments. Since energy has quadratic dependence on field strength, the appearing cross-terms result in 3-body interactions. The force field is no longer pairwise additive, as it includes the interaction energy of the molecule A with dipoles on the molecule B, induced by the molecule C. However, if no mutual polarization is considered, this model is three-body additive. Accounting for back polarization will introduce many-body effects.<sup>7</sup>

In some implementations both polarizabilities and magnitudes of PCs are

considered empirical parameters. In such a case these parameters absorb inaccuracies introduced in other parts of the potential function. A more rigorous approach requires the use of accurate molecular electric properties. The reasonable choice of polarizable centers makes the polarizable model transferable at least for some classes of molecules.<sup>8</sup> The non-pairwise (cooperative) feature of polarization means that it can play a crucial role in reducing intermolecular separation with increasing aggregation. This is important for construction of the force fields suited for both small clusters and condensed phases. However, accounting for polarization will be efficient only if it is the primary reason for the change in molecular electronic structure.<sup>7</sup>

Another way to describe polarization, called fluctuating charge, was suggested by Berne, Freisner et al.<sup>9,10</sup> In this approach atomic charges are considered to be variables, depending on molecular environment. Parameterization is done by electronegativity equalization<sup>11,12</sup> (which was modified to emulate *ab initio* results). However, there are cases (such as the out-of-plane polarization of a planar molecule or of a bifurcated H-bond to oxygen),<sup>10</sup> where a PC-only model is not sufficiently flexible. This made necessary the introduction of inducible atomic dipoles.<sup>13</sup> It is, however, possible to retain an attractive and efficient PC scheme by using several point charges close to the atomic position. A model containing nine PCs for each heavy atom was constructed by Clark and Rauhut.<sup>14</sup> The positions and magnitudes of the charges are associated with centroids of each lobe of the natural atomic hybrid orbitals, which eliminates any fitting. A procedure involving numerical integration of the Slater-type functions was incorporated into the semiempirical package VAMP.<sup>15</sup>

Another approach is to keep the magnitude of the charge constant, but to allow the position of the charge to vary. This possibility will be further discussed in Chapter 6.

We should note here that any model including PC needs to explicitly account for long-distance interactions. By contrast, models including only distributed dipoles (and higher multipoles) allow for small cutoff radii.<sup>16</sup> In Chapter 7 we will show, that one has to include interactions at 50 Å in order to obtain convergence in electrostatic energy. Fortunately, the fast multipoles methods have recently been developed to avoid this problem.<sup>17</sup>

Precise intermolecular force fields have to be individually constructed for each molecule. They are usually based on supermolecule or on intermolecular perturbation theory calculations. The latter are used more often, as IMPT gives separate values for exchange, polarization, and dispersion terms, whereas supermolecule calculation gives only total interaction energy. Some of the examples will be mentioned later in this Chapter. It is necessary to note that perturbation theory treatment beyond the second order yields nonadditive terms not only in the electrostatic components of the energy but also in dispersion attraction and exchange repulsion.<sup>18</sup>

## **2.2 Force-field periodical calculations and prediction of molecular packing**

In typical prediction of crystal structure, hundreds of thousands of starting points are used and hundreds of energy evaluations are necessary for optimization

from each of these starting points. Such a large number of energy evaluations make direct application of MO methods to the problems of this kind impractical. The conventional approach here is to represent the energy by an analytical function with adjustable parameters (create a force-field) and perform optimization of that function.

Whereas optimization of molecular crystal structure using empirical potentials is not a problem, it is much more difficult to predict this structure *a priori*. The very possibility of organic crystal structure prediction is still uncertain.<sup>1</sup> There are several reasons for these difficulties: (a) The shape of a potential surface is complex, with multiple local minima. The complexity here is close to the problem of protein folding. (b) Kinetics may play an important role in crystallization, so that the real structure may not be the global minimum on the potential surface. (c) Empirical force fields may be well fit to represent one region of the potential surface, but not the others. Despite the difficulties, several attempts have been made to predict crystal structures.<sup>19</sup> At present, there are two major approaches to crystal structure prediction. The first could be briefly described as stepwise increasing dimensionality. This method was introduced and used for analog simulations by Kitaigorodskii (*aufbau* algorithm).<sup>1</sup> Gavezzotti later published the computer program PROMET, based on similar ideas.<sup>20</sup> The program optimizes finite-size molecular clusters with the constraints of single crystallographic symmetry operations (including translations, screw axes, and glide planes). The optimization is repeated, starting with different operation or different orientation of the molecule with respect to the symmetry operation. The final geometry represents finite or 1D-cluster. The structures corresponding to the lower energy are

accepted as rigid units to the next step, where 2D-clusters are built. The best structures are used on the third step to build 3D-structures. After final 3D-optimization, a few hypothetical crystal structures are obtained. Unfortunately, only structures with one molecule in an asymmetric unit are considered in PROMET. Successful applications of this program have, however, been published.<sup>21</sup> We will adopt this step by step dimensionality increase for our cluster calculations.

Another approach was introduced by Gdanitz<sup>22</sup> and employs brute computer force. The first step is Monte-Carlo sampling of the configuration space (made of unit cell parameters, molecular center coordinates, orientations, and internal rotation angles for all independent molecules). The second step includes rough optimization and filtering out equivalent structures. In the third step simulated annealing is used to get rid of the shallow minima. Finally, after fine optimization and filtration, a set of nonequivalent polymorph structures is obtained. The final version of the software became the POLYMORPH module in the Cerius<sup>2</sup> package,<sup>23</sup> commercially available from MSI. A program based on a similar approach is called UPACK<sup>24</sup> and uses a regular grid instead of Monte-Carlo sampling in the configurational space. In principle, if the search starts with a large enough unit cell in P1 group, all space group symmetries may be obtained. However, because of computer time considerations the search is restricted to the most common space groups.

Finally, another program by Perlstein, called PACK,<sup>25</sup> which is commercially available from Chemical Design Inc., applies Monte-Carlo sampling and simulated annealing to construct low-dimensional periodical structures. This combines the two

approaches described above. The reduction of dimensionality makes it practically possible to treat of up to three symmetrically independent molecules with up to twelve intramolecular degrees of freedom. The program has been successfully applied to the packing of polymer chains and monolayers.<sup>26</sup> Some new programs,<sup>27</sup> as well as new versions of older programs such as LMIN<sup>28</sup> and others, perform a single 3D-optimization in which the predicted crystal structure depends on the starting point used.

Some of the latest crystal packing suites, such as MPA by Williams<sup>29</sup> and GULP by Gale,<sup>30</sup> have the option of optimizing finite clusters, as well as 1,2,3D-periodicals, and of fitting force field parameters to the set of experimental data.

### **2.3 *Ab initio* and semiempirical periodical calculations**

Fortunately, even optimization with an arbitrary force field (like solid spheres) leads in most cases to a reasonable crystal structure because of the close packing of organic molecules. To obtain a correct energy for this structure, more precise (and computationally expensive) MO methods could be applied. Historically, Crystal Orbital calculations of solid state were undertaken using (oversimplified) semiempirical zero-overlap non iterative approximations based on hybrid atomic orbitals, such as tight-binding<sup>31</sup> and Fenske-Hall<sup>32</sup> models. On the other hand, metals (as opposed to covalent crystals) were historically treated using electron gas models, from which density function theory was eventually developed. Some examples of



computer programs that implement non-iterative methods are YAeHMOP,<sup>33</sup> the extended Hückel method (suitable for CO calculations but not for geometry optimization), and VEH<sup>34</sup> (parameterized to reproduce bond lengths in 1D-polymers). Though computationally light, these models still attract some attention as linear scaling methods for large systems and MD simulations.<sup>35</sup> The introduction of various population-dependent iterative schemes into these methods allows one to build semiempirical DFT schemes.<sup>36</sup> Unfortunately, standard semiempirical packages are not well suited to 3D-periodical calculations (if implemented). For instance, MOPAC6<sup>37</sup> (which has 3D-capability, and not only 1D-, as it is stated in the manual) uses only one point for integration in the Brillouin zone and therefore needs the generation of a large supercell in order to give reasonable results.

Recent advances in DFT methods, such as gradient corrections to exchange-correlation functional and hybrid functionals including exact HF exchange, have made possible the accurate description of H-bonding. For instance, these methods were reported to give the interaction energies for the water dimer as good as or better than second order Møller-Plesset (MP2) calculations.<sup>38,39,40</sup> While electron-correlation is accounted for in DFT methods, these methods have not been successful in calculating dispersion interactions,<sup>41</sup> which makes them an imperfect tool for the study of organic crystals. In this work we used two hybrid functionals: the B3PW91 method combining Becke's 3-parameter functional<sup>42</sup> with the non-local correlation provided by the Perdew-Wang expression,<sup>43</sup> and B3LYP, combining the same Becke functional with the correlation functional of Lee, Yang and Parr.<sup>44</sup>

Most of the modern DFT packages, although they allow optimization and even molecular dynamics (MD) calculations on solid state systems, still use plane wave basis sets, and this makes comparison with molecular MO calculations rather difficult. Although the plane-wave basis set is more suitable for description of highly delocalized electronic structures typically found in metals, molecular crystals are described reasonably well. The recent MD study of HBr crystal phases at high pressure<sup>45</sup> employing the program CPMD<sup>46</sup> reproduced orientational ordering, symmetrization of H-bonds, transition from the FCC to the HCP, and molecular dissociation as the pressure increased.

Among the packages that implement plane-wave DFT treatment, are VASP,<sup>47</sup> CP-PAW,<sup>48</sup> FHIMD98,<sup>49</sup> and CASTEP.<sup>50</sup> To allow the comparison, some of the packages (Wien95,<sup>51</sup> and ADF<sup>52</sup>) offer plane-wave calculations for isolated molecules. To date, only a few programs use atom-centered gaussian basis functions, usual for MO calculations: DMol3<sup>53</sup> (DFT only), PLH<sup>54</sup> (1D-periodicals only), GAPSS,<sup>55</sup> and CRYSTAL<sup>56</sup> (DFT and HF calculations). CRYSTAL can be used to perform infinite periodic calculations in three (crystals), two (slabs), one (polymers), or zero (molecules) dimensions. The periodic nature<sup>57</sup> of the calculations dictates certain approximations, as well as certain basis sets. In our calculations, described in Chapter 3, we chose the 6-21G\*\* basis set, as it is also a standard GAUSSIAN<sup>58</sup> basis set and similar to the 6-31G\*\* basis set generally used. The use of better basis sets for 3D-periodical calculations, including more diffuse primitive gaussian functions with exponent factors below 0.2 (not necessarily A+@ functions), often results in SCF

convergence problems,<sup>59,59a</sup> due to pseudo linear dependence. Unfortunately, the procedure of eliminating linear dependent functions from the basis set, implemented in GAUSSIAN 98, was not yet incorporated into CRYSTAL. As analytical derivatives are not available in CRYSTAL 95/98, geometry and basis set optimizations, as well as frequency calculations can be done numerically using a Unix shell script.<sup>60</sup> This is feasible for systems with only a few geometrical variables, like ice VIII.<sup>41</sup>

A major disadvantage of using the gaussian basis set for Crystal Orbital calculations is basis set superposition error (BSSE). The essence of BSSE is the nonphysical stabilization of one molecule in the presence of basis functions located on the other molecules in the system. The BSSE is particularly large for small basis sets, but vanishes upon approaching complete-basis limit. In supermolecule calculations, the customary (but controversial<sup>61</sup>) way to account for BSSE is counterpoise (CP) procedure:<sup>62</sup>

$$CP = E(A, \text{basis } A) - E(B, \text{basis } AB) + E(B, \text{basis } B) - E(B, \text{basis } AB)$$

All energies should be calculated in the geometry optimal for the dimer, if the optimization is performed.<sup>63</sup> It was shown,<sup>64</sup> that generalization for larger clusters does not give unique results (which is sometimes regarded as a Dannenberg-Turi paradox), unless one uses the sum of individual CP corrections calculated for each monomer in the basis of all monomers in the cluster:

$$CP(M) = E(M, \text{basis } M) - E(M, \text{basis } M_n)$$

CP procedure was recently extended by Duran, Dannenberg et al.<sup>65</sup> to gradients and Hessians using consecutive executions of GAUSSIAN from the Unix shell script,

which allows for geometry optimization on BSSE corrected potential energy surfaces.

There are at least two other alternatives to BSSE corrected optimizations. One is the SCF-MI method introduced by Gianinetti, Raimondi et al.<sup>66</sup> And implemented in GAMESS-UK,<sup>67</sup> which modifies SCF equations to keep MOs localized on different monomers. The resulting wavefunction is close to an artificial state with charge transfer turned off, which was built in Kitaura-Morokuma<sup>68</sup> analysis (electrostatic, polarization, and exchange interactions remain). To bring back this meaningful part of intermolecular interaction, it was suggested to explicitly correlate the orbitals that form H-bonds via valence-bond formalism.<sup>69</sup> Mayer's Chemical Hamiltonian method<sup>70</sup> modifies the Fock matrix to exclude elements responsible for BSSE. It was implemented<sup>71</sup> in the POLYGAUSS program for periodical *ab initio* calculations. An alternative method for BSSE elimination at MP2 level, based on local MP2 treatment, was recently developed and implemented in the MOLPRO package by Werner, Schutz et al.<sup>72</sup> Full CP corrected optimization for the HF part of the energy is implemented in the latest version of this program.

Since full CP is impossible for the infinite crystal, only basis functions of the nearest atoms are used for CP calculations in CRYSTAL.<sup>55</sup> Our attempts to find the distance limit to select the nearest neighbors run into limitations in computational resources sooner than convergence in CP values was reached. In most cases CP evaluations were computationally more expensive than the 3D-calculation itself. A possible solution to this problem is to select only those basis functions that have sizable amplitude on the atoms of the monomer.

Post-HF periodical calculations have also been published, including the MP2/MP4 study on layers of formamide (using POLYGAUSS),<sup>73</sup> chains of water molecules<sup>74</sup> and HCN crystals<sup>75</sup> (using customized algorithms). Coupled-cluster (CC) methods were applied for 1,2D-systems of He atoms and implemented in the PNO-CEPA code.<sup>76</sup> Analytical derivatives for 1D-periodical systems made possible frequency calculations on chains of HF molecules.<sup>77</sup> Analytical first derivatives for 2,3D-periodical systems were also derived.<sup>78</sup> Periodical capability is expected to be added to the CC code ACES II, and to the HF/DFT part of GAUSSIAN 2000.

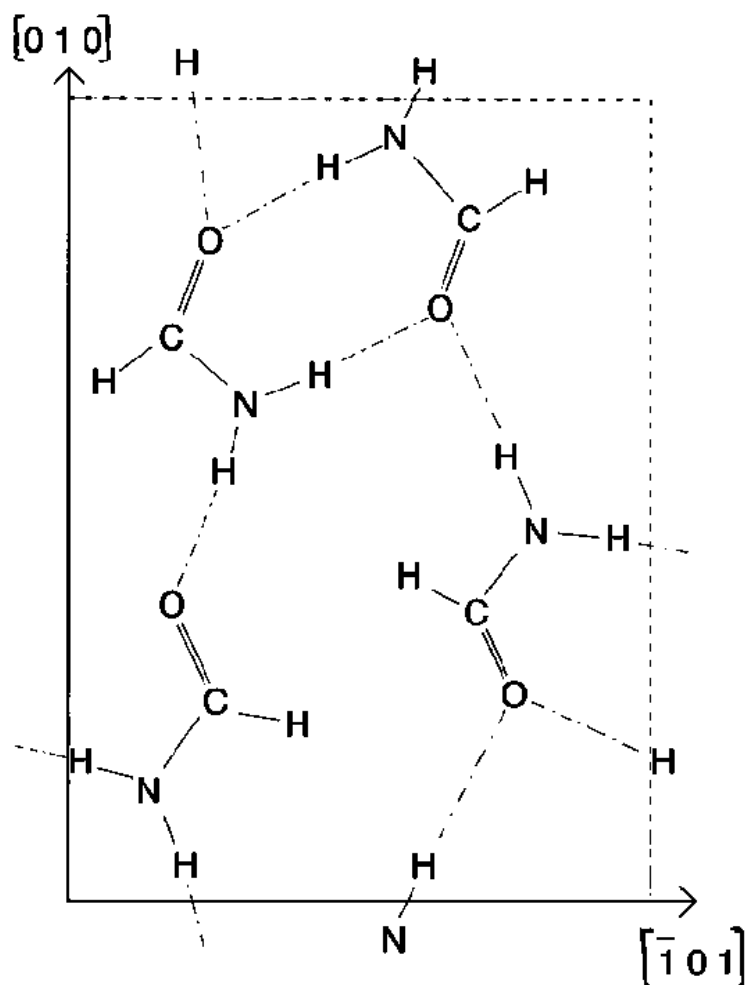
## 2.4 *Ab initio* cluster calculations

Another approach to the theoretical description of the crystals is applied in cluster calculations. The crystal environment of the molecule is usually simulated by point charges (PC)<sup>79</sup> and/or by a finite (usually small) number of neighboring molecules<sup>80</sup> (supermolecule calculations). Earlier approaches assumed pairwise additivity and estimated lattice energy as the sum of dimeric interactions.<sup>81</sup> We will assess the limitations of this approach in Chapters 3 and 5. A combined PC/supermolecule approach is consistently used by Van Alsenoy et al.<sup>82</sup> They have been able to perform optimizations and frequency calculations on relatively large clusters (15 molecules) using a multiplicative integral approximation that treats four-center integrals as a linear combination of three-center integrals. This approach is implemented in the BRABO package. The cluster is embedded in a field of point

charges representing a finite number (usually hundreds) of distant neighbors. As Madelung sums are known to converge slowly, even hundreds of distant neighbors may not be enough to simulate the infinite crystal environment. This is why a special fitting procedure for the values and positions for the limited number of point charges designed to efficiently simulate infinite crystal seems to be useful.<sup>83</sup>

Unfortunately, the point charge method has certain limitations. Sublimation energies were not considered in the papers referenced above and are not well evaluated by point charges method even with the nearest neighbors taken into account explicitly. Also, only the crystal field effects on intramolecular geometry and vibrational frequencies were studied. Intermolecular geometry was not optimized. A wider range of properties can be evaluated if isolated (or implicitly solvated) molecular clusters are considered.

Probably the most attention was paid to study of the water clusters. Here we briefly mention just one paper, since OH...O bonds are not considered in our study. Water cyclic clusters up to the hexamer were optimized<sup>84</sup> at HF and MP2/aug-cc-pVDZ and TZ level of theory, and many-body effects in the interaction energy were analyzed. Three-body effects were found to be up to 30% of the total interaction (depending on the point on a potential surface), whereas four-body and higher order terms were found negligible. Correlation correction was found to account for a 10-20% increase in two-body terms and for a 75% increase in three-body terms.



**Figure 2.1.** 2D H-bonded network in crystal structure of formamide. Cyclic H-bonded dimeric units are joined by H-bonds in a pucker layer. Alternative description: zigzag chains of the molecules parallel to Y-axis are connected by cyclic H-bonds. Reproduced from ref. 85.

A comparisons of cluster and periodical HF, DFT, and MP2/MP4 calculations (with total optimization of geometry) was recently done by Suhai<sup>85</sup> on the example of formamide. The molecular and crystal structures of this compound are closely related to those of urea (Figure 2.1), so the obtained results are important for our study. The results showed C=O and N-H bond elongation, and C-N shortening upon H-bond

formation. At all levels, the energy of the last H-bond in the infinite chain of head-to-tail structure was 60% greater than in the dimer, due to cooperative effects. However, the formation of 2D-infinite structures leads to weakening of the H-bonds in the cyclic dimeric units, compared to isolated dimers. The author found, that convergence of geometrical and energetic parameters is slow (even pentamer recovers only 60-70% of the energy changes observed between the dimer and the infinite chain). The basis set was found to have greater effect on DFT results than on those for HF and even MP2. The TZ(2d,2p) basis was necessary to achieve agreement with the experimental bond lengths. BLYP was found to agree with the MP2 results better than many other DFT functionals (including B3LYP).

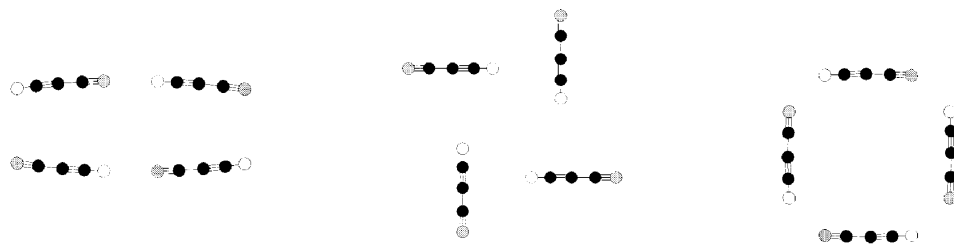
Intermolecular perturbation theory was also applied to formamide dimers.<sup>86</sup> Five minimum energy conformations were found, with the cyclic centrosymmetric dimer being the most stable. An accurate polarizable potential was constructed to reproduce these results. When this potential was applied to calculate clusters up to eight molecules, the last H-bond in the linear clusters was found to have 25% cooperativity. The preference of linear chains over cyclic dimers in the liquid phase<sup>87</sup> was attributed to this cooperativity.

Linear chains  $(\text{HCN})_n$ ,  $n=2-7$  considered by King and Weinhold<sup>88</sup> are other examples of cluster calculations. 40% of the last H-bond energy in the heptamer at HF/6-31+G\* level was found to be due to cooperativity. An average dipole moment per molecule was found to increase from 3.3 D for the monomer to 3.6 D for the dimer, to 4.1 D for the heptamer. The calculation results agree well with geometrical



parameters, and with vibrational and nuclear quadrupole resonance spectra. No comparison with crystals or periodical calculations was made. Employing the nonpolarizable electrostatic model, and considering the interactions only between the nearest neighbors, the authors argued that only a charge transfer can give a correct description of the cooperative effects. In a comment on this paper, a quantitative electrostatic description including distributed atomic multipoles and polarizabilities for the same system was used by Stone and Buckingham.<sup>89</sup> These authors showed that nonpolarizable treatment yields 15% of the last H-bond strength cooperativity due to distant interactions. If polarization is included, 30% cooperativity is obtained. The average dipole moment per molecule was found to increase from 3.0 D for the monomer to 3.4 D for the dimer to 3.8 D for the octamer. Similar results were obtained with a polarizable force field constructed to reproduce IMPT results for HCN dimers: 27% cooperativity, and dipole moment from 3.0 D for the monomer to 3.3 D for the dimer to 3.7 D for the octamer.<sup>90</sup> In an *ab initio* study by Karpfen,<sup>91</sup> both linear and cyclic clusters of hydrogen cyanide and cyanoacetylene up to decamers were examined at HF, B3LYP, and MP2 levels with different basis sets. Cyclic clusters (Figure 2.2) were found to exhibit stronger cooperativity (up to 70%) and to be more stable beginning from tetramer for both species. This is an opposite trend to the one observed from the formamide clusters described above. Stacking clusters with parallel and antiparallel orientations of cyanoacetylene molecules, typical of crystals, were found<sup>92</sup> to have stability comparable to that of cyclic clusters.

A similar energy preference of cyclic to linear clusters was found in an MP2/6-



**Figure 2.2.** Structures of cyanoacetylene tetramers: antiparallel stacking arrangement of two linear dimers (left), pinwheel structure (center), and cyclic structure (right). Reproduced from ref. 90.

31+G\*\* study on trimers consisting of methanol and water molecules.<sup>93</sup> A donor-acceptor orbital description was again used to rationalize these results. The authors referred to an earlier study<sup>94</sup> of water trimers, in which many-body polarization effects were able to recover only 60% of non-additivity. In another MP2/6-311++G\*\* study on trimers consisting of methanol and trifluoromethanol<sup>95</sup> cooperative effects were found for both energies, H-bonding distances, O-H bond lengths, shifts in the stretching frequencies of the donor O-H bond, and electronic charge densities at the bond critical points. Similar cooperative effects on these properties were also found in a B3LYP/6-311G\*\* study of ethanol<sup>96</sup> and 1-propanol<sup>97</sup> clusters.

Clusters of up to four molecules of methylamine were considered in another study.<sup>98</sup> At HF, B3LYP, and MP2/6-31+G\* levels non-additive contribution to the interaction was found to be in the range of 12-18%. N-H distances and vibrational frequencies were found to change with the cluster size, in accord with the gas phase experimental data.

*Ab initio* cluster calculations were also found useful for statistical thermodynamic evaluation of the physical properties and spectra of liquids by means of Quantum Cluster Equilibrium theory, as shown in the example of N-methyl formamide.<sup>99</sup> In this theory the equilibrium populations of the dimers, trimers,..., hexamers were evaluated at a certain temperature based on *ab initio* calculated interaction energies for each cluster. This approach allows one to derive the equation of state for liquids and non-ideal gases and to describe phase transitions. However, it is limited to equilibrium phenomena. Kinetics and non-equilibrium phenomena require molecular dynamics simulations, when individual trajectories of nuclei are described classically or semiclassically. As the size of the system in the MD approach must be sufficient to simulate long-distance disorder, *ab initio* treatment is too expensive in most cases. At present, MD simulations are done at the empirical force field level (with or without polarizable potentials). The search for inexpensive methods for improving the results of MD simulations includes some variations of the simplified cluster approach. This would describe the electronic structure of the system on each step of the nuclear motion (Aon the fly<sup>®</sup>), instead of calculation potential energy function before the calculation. For example, a modification of the valence bond method named Adiatomics-in-molecules<sup>®</sup> applied to (HF)<sub>n</sub>, n=3-6 system was shown to give energies for sixteen cluster conformations closer to MP2/6-311+G(2d,2p) results than to those achieved using a polarizable force field.<sup>100</sup> Unfortunately, the diatomics-in-molecules method treats the contributions of ionic states as empirical parameter. Using the same parameter for the different molecules in a cluster and for clusters of

different size is likely to underestimate cooperative effects.

Imposing translational symmetry can significantly simplify large cluster calculations. In HF calculations of large (500 heavy atom) clusters of diamond and ZnS<sup>101</sup> translational symmetry allowed one to reduce the number of necessary integrals. Even periodical constraints on intra- and intermolecular geometrical parameters help to achieve convergence in cases too large for full optimization. Such calculations were performed by Dannenberg and Turi on clusters of acetic acid,<sup>102</sup> cyclohexane-1,3-dione,<sup>103</sup> and nitroanilines.<sup>104</sup> However, the relative stability of organic polymorphs has not been studied at *ab initio* level. Comparison of two polymorphic structures could reveal a predictive strength of cluster calculations, using no empirical parameters. This explains our interest in the systems described below.

## **2.5 Urea molecular structure and vibrational spectra in the gas phase and in crystals**

Urea and thiourea provide interesting and contrasting examples of how small changes in molecular structure can have a large influence on crystal structure.

Investigating the basis of these effects can be of singular importance for understanding and designing intermolecular interactions that dictate crystal packing. This understanding will eventually play important role in crystal engineering.

Urea crystals attract the attention of both theoreticians and experimentalists

due to their nonlinear optical and piezoelectric properties.<sup>105</sup> The intermolecular interactions of urea molecules with water<sup>106</sup> and with hydrophobic molecules<sup>107</sup> have received much attention in connection with protein denaturation and RNA folding.<sup>108</sup>

Most chemists have assumed that urea is a planar symmetrical molecule. Indeed, the crystal structures that have been published have reinforced this assumption (see Figure 2.5). Below we will refer to the most precise low temperature (12K) neutron study by Swaminathan et al.<sup>109</sup> Moreover, Bowen,<sup>110</sup> Coussens,<sup>111</sup> Frenking,<sup>112</sup> and Dixon<sup>113</sup> have recently published theoretical studies of urea using *ab initio* and DFT calculations up to MP4/6-311G\*\*//MP2/6-31G\*. These studies show the parent molecule to be nonplanar. The planar structure was reported to be a second order saddle point connecting the two pairs of equivalent nonplanar minima. In fact, the nonplanarity of urea had previously been suggested by King in his early vibrational analysis of urea in an argon matrix.<sup>114</sup> We will refer to that paper below as the matrix isolation experiment. Although several groups were aware of the reported nonplanarity of urea, analyses of experimental vibrational and microwave spectra have assumed planarity for simplicity. Only recently have these data been reassigned based on possibly nonplanar conformational behavior. Gas microwave experimental data on the geometrical parameters of nonplanar urea molecules were reported by Godfrey,<sup>115</sup> and will be referred below to as MW data.

The most comprehensive study to date, that of Van Alsenoy et al.<sup>116</sup> deals with the geometry and spectra of the urea molecule in the gas and in crystal phases. It reports the results of HF/6-31++G\*\* calculations for the free molecule and the

**Table 2.1.** Comparison between calculated (HF/6-31++G\*\*) and experimental (MW in the gas,<sup>115</sup> and ND in the crystal phase<sup>109</sup>) bond lengths (Å), valent and dihedral angles (°) for the gas phase and the crystal phase of Urea. Reproduced from ref. 116.

	gas			crystal			gas vs. crystal	
bonds	r <sub>e</sub> , calc.	r <sub>s</sub> , MW	Δ	r <sub>e</sub> , calc.	r <sub>α</sub> , ND	Δ	calc.	exp.
CO	1.200	1.221	-0.021	1.242	1.265(1)	-0.023	0.042	0.044
CN	1.370	1.378	-0.008	1.331	1.349(1)	-0.018	-0.039	-0.029
NHs	0.999	1.021	-0.022	0.999	1.008(4)	-0.009	0.000	0.013
NHa	0.998	0.998	0.000	0.999	1.001(4)	-0.002	0.001	0.003
angles								
OCN	122.7	122.6	0.1	121.2	121.4(1)	-0.2	-1.5	-1.2
NCN	114.6	114.7	-0.1	117.6	117.2(1)	0.4	3.0	2.5
CNHs	114.1	112.8	1.3	119.3	119.1(1)	0.2	5.2	6.3
CNHa	118.7	119.2	-0.5	120.9	120.5(1)	0.4	2.2	1.3
HsNHa	115.3	118.6	-3.3	119.8	120.4(1)	-0.6	4.5	1.8
dihedrals								
OCNHs	-12.5	-10.8	-1.7	0	0	0	12.5	10.8
OCNHa	-153.7	-156.9	3.2	-180	-180	0	-26.3	-23.1
NCNHs	167.5	169.2	-1.7	180	180	0	12.5	10.8

for the molecule in the crystal environment (simulated by the 14 nearest neighbors, with 664 neighbors represented by point charges). In this environment, the molecule becomes planar. The comparison between calculated and experimental data (gas microwave<sup>108</sup> and crystal neutron diffraction<sup>102</sup> at 12K) is summarized in Table 2.1. HF calculations predict the correct trends in geometrical changes between the gas and crystal phases. The bond lengths are 0.01-0.02 Å shorter than experimental values. Valence and torsional angles are within 3° range of experiment (0.6° for crystal phase).

**Table 2.2.** Experimental (MW) rotational constants (MHz) and differences between experimental and calculated values obtained using the experimental  $r_s$  and calculated  $r_e$  structure.

	MW	$\Delta$ , exp	$\Delta$ , HF/6-31++G**
(NH <sub>2</sub> )CO(NH <sub>2</sub> )			
A	11,233	20	285
B	10,369	28	142
C	5,417	16	118
(NH <sub>2</sub> )CO(NHD)			
A	11,225	24	287
B	9,590	23	130
C	5,197	15	111
(NH <sub>2</sub> )CO(NDH)			
A	10,826	28	253
B	9,895	21	150
C	5,204	14	112
<sup>15</sup> (NH <sub>2</sub> )CO( <sup>15</sup> NH <sub>2</sub> )			
A	11,027	19	279
B	9,828	25	134
C	5,220	15	112
(NH <sub>2</sub> )C <sup>18</sup> O(NH <sub>2</sub> )			
A	10,466	17	264
B	10,369	28	142
C	5,231	16	115

Calculated rotational constants are compared to experimental values in Table 2.2.

They are about 3% too small. After the authors empirically corrected the calculated structure to shorten C=O and C-N bonds, the agreement became quantitative.

The gas phase vibrational spectrum of urea is hard to obtain due to the quick thermal decomposition of urea at sublimation temperature. Only one gas-phase spectrum, that of Langer et al,<sup>117</sup> has been published. Vibrational spectra in the solution were studied repeatedly, and we will refer below to the detailed IR study in acetonitrile by Hadzi.<sup>118</sup> The most comprehensive spectroscopic study in crystal phase was published again by Van Alsenoy.<sup>119</sup> This study combines Infrared and Raman spectra of solid urea at high pressure (up to 1 GPa) and low temperature (-196°C), with cluster frequency calculations. The comparison of experimental and calculated frequencies is presented in Tables 2.3-2.4. While comparing calculated and experimental frequencies for urea, the authors<sup>119</sup> had to introduce individual scaling factors for crystal and gas. In addition, they used individual scaling factors for the N-H stretch in the gas phase and for the C=O stretch in the solid phase, in order to get satisfactory agreement.

The changes in observed frequencies correspond to the weakening of N-H and C=O bonds and to the strengthening in C-N bonds from gas to solution to crystal at room temperature (Figures 2.3a-c) to crystal at low temperature (or to crystal at high pressure). Also, NH<sub>2</sub> rocking vibrations shift to a lower frequency and NH<sub>2</sub>



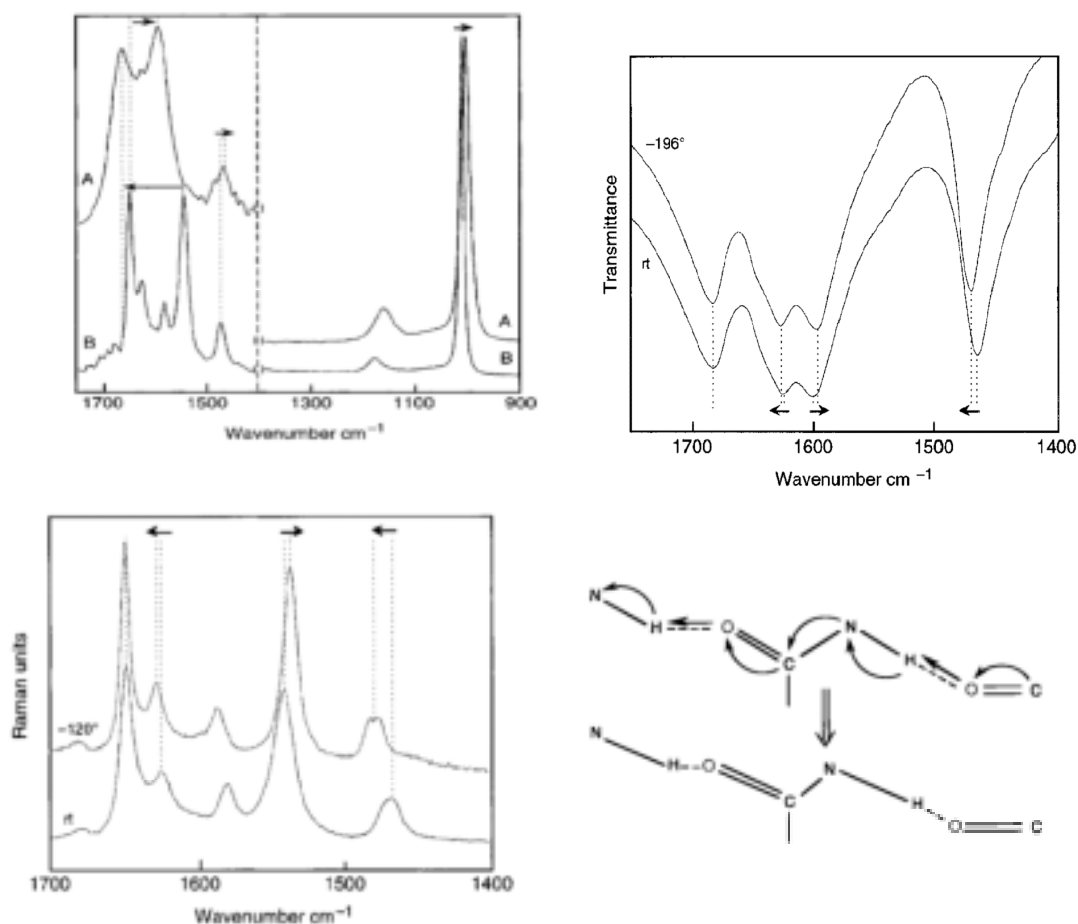
**Table 2.3.** Vibrational frequencies for urea and deuterated urea molecules: experimental (solution, Ar matrix isolation, and gas-phase), calculated (HF/6-311++G\*\*, two scaling factors), and difference between calculated and experimental (matrix isolation),  $\text{cm}^{-1}$

		$^1\text{H}$					$^2\text{D}$		
assignment	S	soln.	matr	gas	calc.	$\delta$	matr.	calc.	$\delta$
$\nu_a(\text{NH}_2)$	A	3503	3548	3533	3542	-6	2648	2623	-25
$\nu_a(\text{NH}_2)$	B	3503	3548	3559	3541	-7	2648	2620	-28
$\nu_s(\text{NH}_2)$	A	3390	3440	3434	3425	-5	2505	2485	-20
$\nu_s(\text{NH}_2)$	B	3390	3440	3460	3431	-9	2505	2480	-25
$\nu(\text{CO})$	A	1695	1734	1776	1731	-3	1723	1707	-16
$\delta_a(\text{NH}_2)$	B	1614	1594	1749	1600	6		1135	
$\delta_s(\text{NH}_2)$	A	1614	1594	1604	1589	-5	1223	1219	-4
$\nu_a(\text{CN})$	B	1419	1394	1394	1386	-8	1408	1407	-1
$\rho_s(\text{NH}_2)$	A	1167		1157	1149			968	
$\rho_a(\text{NH}_2)$	B	1167	1014	1157	1027	13		839	
$\nu_s(\text{CN})$	A	969	960	1023	934	-26	845	830	-15
$\omega(\text{CO})$	B		790	775	785	-5		756	
$\delta(\text{CO})$	B	576	578	572	567	-11	517	512	-5
$\omega_s(\text{NH}_2)$	A				518			410	
$\tau_a(\text{NH}_2)$	B	509			516			322	
$\delta(\text{CN})$	A				466			390	
$\omega_a(\text{NH}_2)$	B		410		422	12		377	
$\tau_s(\text{NH}_2)$	A				347			247	

**Table 2.4.** Crystal-phase experimental and calculated frequencies ( $\text{cm}^{-1}$ ) for urea and deuterated urea.

		$^1\text{H}$			$^2\text{D}$		
assign.	S	$\nu_{\text{exp}}$	$\nu_{\text{calc}}$	$\delta$	$\nu_{\text{exp}}$	$\nu_{\text{calc}}$	$\delta$
$\nu_{\text{a}}(\text{NH}_2)$	A1	3448	3460	12	2595	2573	-22
$\nu_{\text{a}}(\text{NH}_2)$	B2	3435	3452	17	2584	2563	-21
$\nu_{\text{s}}(\text{NH}_2)$	A1	3345	3347	2	2439	2423	-16
$\nu_{\text{s}}(\text{NH}_2)$	B2	3330	3326	-4	2431	2403	-28
$\nu(\text{CO})$	A1	1598	1597	-1	1603	1601	-2
$\delta_{\text{a}}(\text{NH}_2)$	B2	1627	1631	4	1154	1147	-7
$\delta_{\text{s}}(\text{NH}_2)$	A1	1683	1658	-25	1251	1247	-4
$\nu_{\text{a}}(\text{CN})$	B2	1471	1469	-2	1490	1506	16
$\rho_{\text{s}}(\text{NH}_2)$	A1	1149	1153	4	1002	991	-11
$\rho_{\text{a}}(\text{NH}_2)$	B2	1055	1062	7	855	843	-12
$\nu_{\text{s}}(\text{CN})$	A1	1008	1013	5	891	885	-6
$\omega(\text{CO})$	B1	790	797	7	779	787	8
$\delta(\text{CO})$	B2	568	576	8	527	508	19
$\omega_{\text{s}}(\text{NH}_2)$	A2		463			361	
$\tau_{\text{a}}(\text{NH}_2)$	B1	727	730	3	550	533	-17
$\delta(\text{CN})$	A1	532	540	8	466	459	-7
$\omega_{\text{a}}(\text{NH}_2)$	B1	508	512	4	379	388	12
$\tau_{\text{s}}(\text{NH}_2)$	A2		602			428	

deformation and CO wagging vibrations shift to a higher frequency. Therefore, force constants for the urea molecule significantly change in different phases. The use of the gas force constants for solid and solution was responsible for the incorrect assignment of vibrational modes in earlier studies. The changes in the bond strengths were attributed to H-bonding and illustrated using a simple resonance picture (Figure 2.3).



**Figure 2.3** (top left) Raman spectra of urea in aqueous solution (A) and in crystal (B); (top right) Low-temperature shifts in the 1700-1400  $\text{cm}^{-1}$  region of the infrared spectrum of urea; (bottom left) Low-temperature shifts in the 1700-1400  $\text{cm}^{-1}$  region of the Raman spectrum of urea; (bottom right) Effect of H-bonding on the NH, CO, and CN strength (reproduced from Ref. 119)

## 2.6 Structure and spectra for dimers and trimers

To our knowledge, dimerization of urea molecules has only been studied theoretically. In earlier force field and intermolecular perturbation theory studies,<sup>106</sup> two dimers, cyclic and head-to-tail, were usually considered. Molecular geometry was assumed to be planar. Cyclic dimers were found to be the most stable. Their interaction energies of 22<sup>106b</sup> and 20<sup>106d</sup> kcal/mol were obtained from low-level *ab initio* calculations (HF/3-21G, no BSSE correction). Head-to-tail dimeric configuration and two trimers (head-to-tail and transverse, corresponding to **CAB** and **GAF** on Figure 3.4) were considered by Perez and Dupuis.<sup>120</sup> These authors performed single-point HF calculations in order to examine the additivity of (hyper) polarizabilities. Although five basis sets were considered for the monomer (D95 with various number of diffuse and polarization functions), the authors neglected to specify which one was used for cluster calculations. The dipole moment increased from 5.3 D in the monomer to 12.3 D for the dimer to 19.7 D for the head-to-tail trimer (a 25% increase from the monomeric value). For the transverse trimer, where molecular dipole moments are antiparallel and two of them cancel each other, they calculated a dipole moment of 4.5 D (a 15% decrease from the monomeric value). The interaction energy (without CP correction or molecular relaxation) was calculated to be 12.4 kcal/mol for the dimer, 27.8 kcal/mol for the head-to-tail trimer (so that the second H-bond is 25% stronger than the first), and 15.4 kcal/mol for the transverse trimer. The authors found significant cooperative effects of the individual components for polarizability and

hyperpolarizability tensor. However, the average values were additive to a good approximation.

After our present study was concluded, Belosludov, Li, and Kawazoe published a paper on *ab initio* calculations of trimers and dimers.<sup>121</sup> In their work the dimers were optimized using HF, MP2, BLYP, and BPW91 methods with 6-31G, 6-31G\*, and 6-31++G\*\* basis sets. The trimers were optimized at HF, BLYP, and BPW91 levels. Various starting geometries found in the crystal structures were used. Only two stable dimers were found: a head-to-tail dimer with two NH<sub>2</sub> groups of one molecule H-bonded to the O atom of another molecule, with an extra NH...N bond (see dimer **CB0** on Figure 4.2) and a cyclic dimer with two equivalent NH...O bonds (see dimer **R** on Figure 4.2). The interaction energies in these structures were calculated to be 9.0 and 11.5 kcal/mol at HF/6-31++G\*\* level after CP correction. Neither orientation is observed in the experimental crystal structure. The global minimum among trimers consists of two cyclic dimeric units linked via one molecule (**CAB** on Figure 3.5), with interaction energy of 19.1 kcal/mol. Unlike the cyclic dimer, this trimer is planar, which was confirmed by frequency calculations. A similar arrangement (not planar, however) is observed in the hexagonal host structure of urea with different guest molecules (see Figure 2.5), but not in pure crystalline urea.

Considering vibrational frequencies, the authors found that the calculated spectra for the monomer are in agreement with available experimental data. They assigned vibrations at 1439, 1625, and 1700 cm<sup>-1</sup>, experimentally observed for urea in the gas phase to the dimer, and the vibration at 227 cm<sup>-1</sup> to the trimer.

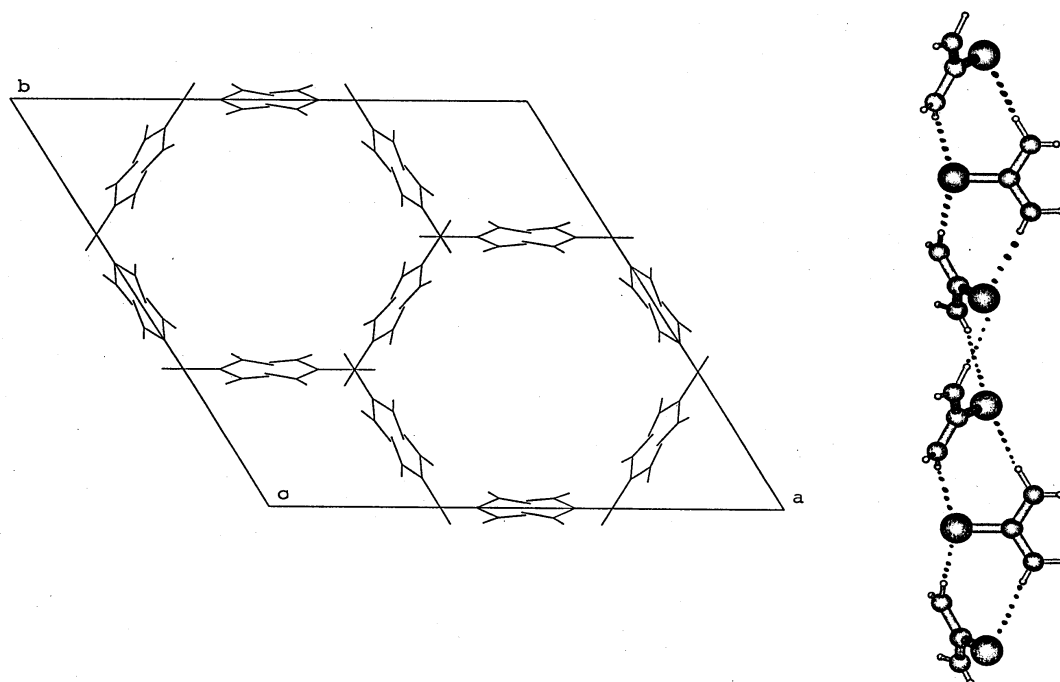
The authors concluded that H-bonding interaction is important for stabilizing planar geometry in small clusters, but not sufficient for forming this geometry in crystals. They noted that the structures of the dimers and trimers are closely related to the hexagonal than to the tetragonal structure of urea in the crystal phase. The results of this paper will be discussed in Chapter 5 in connection with our own results.

## 2.7 Crystal structure of urea not based on the most stable dimer

The crystal structures of urea inclusion compounds were studied in detail.<sup>122</sup> They can be described as spiral ribbons of  $3_1$  symmetry made of cyclic dimers and packed in a honeycomb manner. The linear channels in this structure are occupied by disordered solvent molecules or by other guest molecules which can sterically fit there. This property is well known and is applied in industry to the separation of branched and linear hydrocarbons.<sup>115</sup> The space group of the structure is  $R\bar{3}c$ . Ordering of the guest molecules leads to the loss of the center of symmetry ( $R\bar{3}c$ ), or of the glide plane ( $R\bar{3}$ ), or both ( $R3$ ). The projection of the spiral ribbons on axis X and their packing along the hexagonal axis is shown in Figure 2.4. This structure is typical for inclusion compounds of urea, thiourea and selenourea. The hexagonal polymorphic form of selenourea,<sup>123</sup> crystallizing in the space group  $P3_1$ , is based on this structure. Instead of guest molecules, it has spiral H-bonded thiourea ribbons of  $3_1$  symmetry filling the channels without H-bonding to the host structure. These ribbons distort the honeycomb network so that the body centered translational symmetry is lost and

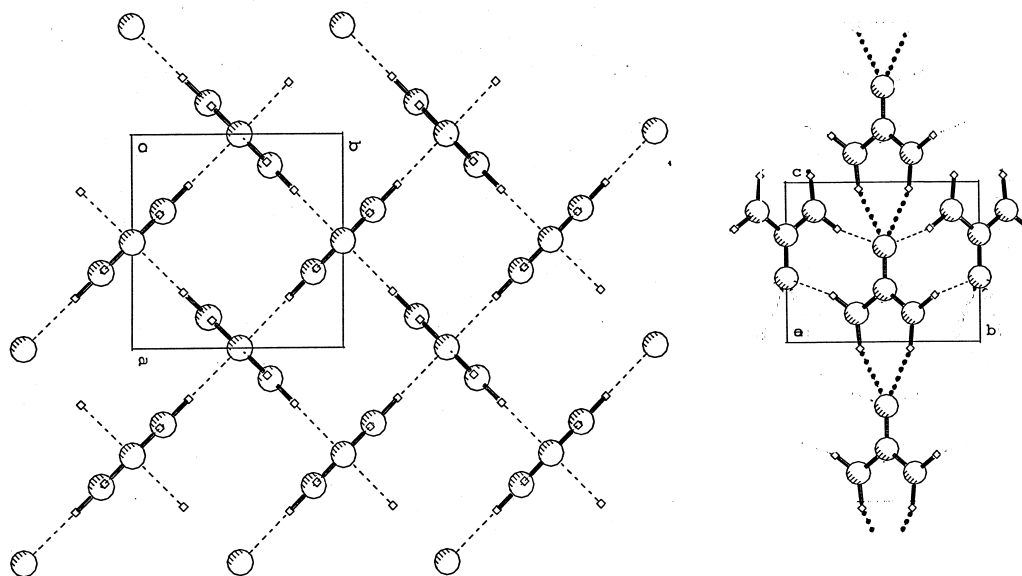
C C D C

Refcode: FABTAD10



**Figure 2.4.** Crystal structure of hexagonal urea host frame from urea-CHCl<sub>3</sub> inclusion compound.

channels become symmetrically-independent. Host spirals are no longer  $3_1$  symmetrical nor equivalent. Consequently, selenourea has nine independent molecules in the asymmetric unit cell -- a record among molecular crystals. However, for urea and thiourea hexagonal structures without guest molecules have never been observed in the experiment. Urea forms a tetragonal structure of  $P-4_2/m$  symmetry (Figure 2.5), in which the molecules form H-bonded chains in a head-to-tail manner. Each molecule uses two hydrogen atoms to form H-bonds with one oxygen atom of the next molecule. The chains are arranged in a herringbone motif, so that each molecule



**Figure 2.5.** Crystal structure of urea in  $P-42_1m$  space group.

donates two H-bonds to two of the neighboring chains and accepts two H-bonds from two other chains. This is the only known structure with four H-bonds to one carbonyl group. Since the direction of the chains alternates, the structure is non polar overall.

The experimental enthalpy of sublimation for crystalline urea was reported to be  $20.95 \pm 0.21$ <sup>124</sup> and  $23.3 \pm 0.24$  kcal/mol.<sup>125</sup> The first attempt to access this value by *ab initio* methods was the periodical HF/6-21G\*\* calculation by Dovesi, Roetti, et al.<sup>126</sup> using CRYSTAL and experimental geometry. The value before CP correction was 33.5 kcal/mol, partial CP correction brings it to 21.4 kcal/mol, and relaxation of the monomer brings it to 16.3 kcal/mol. Due to the difficulties discussed in Section 2.3, only the nearest neighbors, those at a distance closer than 2.5 Å, were taken into



account. In Section 3.5 we will show that using this cutoff one recovers at most 60% of full CP correction. All atomic Mulliken charges were found to increase in absolute value in comparison with an isolated molecule. Bond populations decreased for C=O, and N-H bonds, and increased for C-N and O...H bonds, in accord with the resonance picture (Figure 2.3).

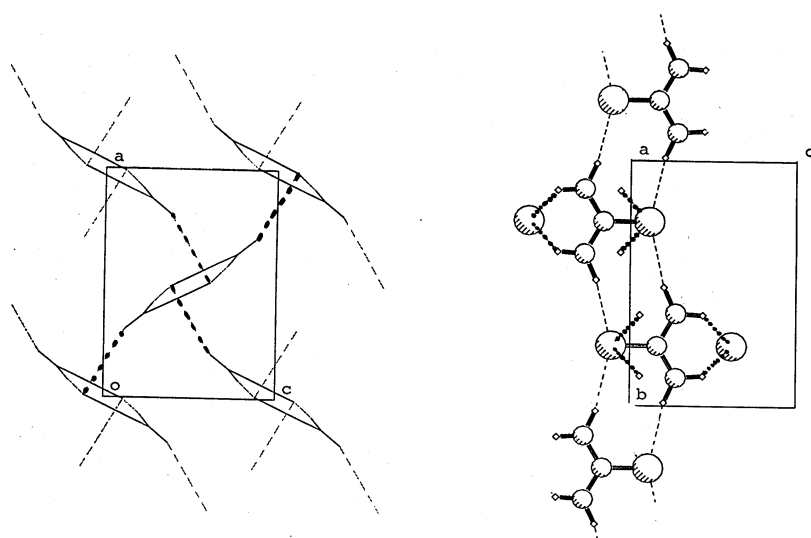
The urea crystal structure was optimized by Van Alsenoy et al. using the non-gradient corrected DFT method in the plane wave basis with pseudopotentials.<sup>127</sup> Instead of total energy, the enthalpy  $H=E+pV$  was minimized for different pressure values. The hydrogen bonds between the chains were found to shorten much faster than those within the chains upon the application of external pressure. Since single molecule calculations were done with a different basis set and a different DFT functional, the heat of formation was not estimated.

The molecular dipole moment of urea shows significant polarization, from 3.83 D in the gas phase<sup>110</sup> to 4.2 D in solution<sup>128</sup> to 4.66 D in crystal.<sup>129</sup> The latter value was obtained from X-rays diffuse scattering measurements interpreted with a model of longitudinal lattice dynamics. We should note that Raman spectra of the lattice vibrations yielded a much smaller value of 3.0 D.<sup>130</sup>

Model calculations show that refinement of atomic multipole moments from high-precision X-ray diffraction data for monocrystals is capable of quantitative retrieval of the electron density redistribution due to intermolecular interaction (interaction density).<sup>131</sup> In fact, experimental electron density distribution in the urea crystal was studied repeatedly by means of X-ray diffraction.<sup>132</sup> The results were

compared to molecular and periodical HF calculations and used to estimate the dipole moment and sublimation enthalpy.<sup>133</sup> For the latter, the classical electrostatic part derived from the interaction of experimental electron densities was supplemented by an empirical a 6-exp force field. This simple scheme, which neglects relaxation and polarization energy of the molecule in the crystal was suggested by Spackman.<sup>133a</sup> It yields 15.7 kcal/mol, surprisingly close to our periodical HF/6-311G\*\* result, reported in Section 3.5. Close agreement between this scheme and the crystal orbital HF result was also obtained by Abramov, Coppens et al. in their study of three crystalline amino acids.<sup>134</sup> The scheme was further improved by Tsirelson, Feil et al.<sup>133b</sup> They introduced an induction energy term depending on the deformation of the molecular electron density upon crystal formation. To obtain this deformation, the HF electron density of a single molecule was subtracted from the experimental electron density. The use of the calculated HF electron density with this improved model yields interaction energy of 21.8 kcal/mol, close to the experimental sublimation energy. However, compared to HF interaction energy this value is highly overestimated. If the experimental electron density is used, the electrostatic interaction is 10 kcal/mol weaker, mostly because of the large differences between experimental and HF monopole populations (atomic charges).<sup>133b</sup> However, the induction energy is calculated to be +7 kcal/mol, a positive value with no physical sense. The authors see the reason for this failure in experimental uncertainties in the phases of the structural factors for non-centrosymmetric crystals,<sup>135</sup> and conclude that experimental interaction density is unreliable in this case. It is interesting to note that, besides experimental errors,

molecular electron distribution depends on the refinement procedure. The dipole moment values reported for the same set of data varied from 3.8 D<sup>132c</sup> to 4.2 D.<sup>133b</sup> A stronger (three-fold) model dependence for molecular dipole moment obtained from X-ray diffraction data was found in the case of 4-nitro-4'-aminobiphenyl.<sup>136</sup>



**Figure 2.6.** Crystal structure of thiourea in *Pmna* space group (high temperature modification).

## 2.8 Thiourea not isomorphic with urea

Unlike urea, thiourea forms orthogonal crystals<sup>137</sup> in space group *Pmna* (Figure 2.6). In these crystals, molecules are linked into ribbons by cyclic dimeric interactions.

These slightly nonplanar ribbons are packed in a herringbone motif. Each molecule forms two H-bonds with other ribbons. At low temperatures thiourea undergoes ferroelectric phase transition to another polymorph,  $P2_1ma$ , which is closely related to this structure.<sup>138</sup> It can be described as a deformed modification, in which the H-bonds between the ribbons are no longer equivalent (one is shorter than the other). As a result, the molecular planes within the ribbon are no longer parallel to each other and the unit cell contains two symmetrically-independent molecules.

The experimental enthalpy of sublimation for thiourea was reported as  $22.4 \pm 2.4$ <sup>139</sup> and  $26.8 \pm 0.36$  kcal/mol.<sup>140</sup> To our knowledge, no previous attempts have been made to simulate this crystal structure with *ab initio* methods.

As one can see, the most stable dimer of urea has nothing in common with its crystal structure. Rather, it is closely related to the crystal structure of thiourea. To resolve this paradox, and to understand the reasons behind the differences in the urea and thiourea structures, we will apply *ab initio* methods, as described in the following Chapters.

## References for Chapter 2.

- <sup>1</sup> Kitaigorodskii, A.I., Organic Chemical Crystallography, Consultants Bureau; New York, **1961**; pp 65-112.
- <sup>2</sup> Hayes, I.C.; Stone, A.J.: Mol. Phys., **1984**, 53, 107.
- <sup>3</sup> Jeziorski, B.; Moszynski, R.; Ratkiewicz, A.; Rybak, S.; Szalewicz, K.; Williams, H. L. In *Methods and Techniques in Computational Chemistry: METECC-94, Vol. B, Medium Size Systems*; Clementi, E., Ed.; STEF: Cagliari, 1993; p 79.  
<http://www.physics.udel.edu/wwwusers/mas/group.htm>
- <sup>4</sup> CADPAC: The Cambridge Analytic Derivatives Package. Amos, R.D.; Alberts, I.L.; Andrews, J.S., Colwell, S.M.; Handy, N.C.; Jayatilaka, D.; Knowles, P.J.; Kobayashi, R.; Laidig, K.E.; Laming, G.; Lee, A.M.; Maslen, P.E.; Murray, C.W., Rice, J.E., Scimandrias, E.D.; Stone, A.J.; Su, M.D.; Tozer, D.J. **1995**;  
<http://ket.ch.cam.ac.uk/software/cadpac.html>
- <sup>5</sup> Meng, E. C., Caldwell, J. W., Kollman, P. A., J. Phys. Chem., **1996**, 100(6), 2367.
- <sup>6</sup> Bursulaya, B.D.; Zichi, D.A.; Kim, H.J.: J. Phys. Chem., **1996**, 100, 1392.
- <sup>7</sup> Dykstra, C.E.: Chem. Rev., **1993**, 93, 2339.
- <sup>8</sup> van Duijnen, P. T., Swart, M., J. Phys. Chem. A; **1998**; 102(14); 2399.
- <sup>9</sup> Rick, S.W.; Berne, B.J.: J. Am.Chem. Soc., **1996**; 118(3); 672.
- <sup>10</sup> Banks, J.L; Kaminski, G.A.; Zhou, R.; Mainz, D.T.; Berne, B.J.; Freisner, R.A.: J. Chem. Phys., **1999**, 110, 741.
- <sup>11</sup> Rappe, A.K.; Goddard, W.A.III: J. Phys. Chem.; **1991**; 95; 3358.
- <sup>12</sup> Allen, L.C.: Electronegativity and the periodic table. In: The Encyclopedia of Computational Chemistry, Ed. Schleyer, P.v.R., **1998**, 3, 123.
- <sup>13</sup> Stern, H.A.; Kaminski, G.A.; Banks, J.L.; Zhou, R.; Berne, B.J.; Freisner, R.A.: J. Phys. Chem., **1999**, 103, 4730.
- <sup>14</sup> Rauhut, G.; Clark, T.: J. Comput. Chem., **1993**, 14, 503; Beck, B.; Rauhut, G.; Clark, T.: J. Comp. Chem., **1994**, 15, 1064.

15. Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Sauer, W.; Beck, B.; Hutter, M.; Clark, T.: **VAMP**, Oxford Molecular  
<http://www.oxmol.com/software/tsar3d/spec.shtml#vamp>
16. Batista, E.R.; Xantheas, S.S.; Jónsson, H.: J. Chem. Phys., **1998**, 109(11), 4546.
17. Board, J.; Schulten, K.: Comput. Sci. Eng., **2000**, 2(1), 76.
18. Lotrich, V.F.; Szalewicz, K.: J. Chem. Phys., **1997**, 106(23), 9668.
19. Gdanitz, R.J., *Theoretical aspects and computer modelling of the molecular solid state*, Ed. Gavezzotti, A., John Wiley & Sons, New York, **1997**, 195.
20. Gavezzotti A., J. Am.Chem. Soc., **1991**, 113, 4622.
21. Braga, D., et. al., J.Chem. Soc, Dalton Trans., **1995**, 1215.
22. Karfunkel, H.R., Gdanitz, R.J., J. Comp.Chem., **1992**, 13, 1171.
23. Verwer, P.; Leusen, F.J.J.: Reviews in Computational Chemistry, K.B. Lipkowitz and D.B. Boyd, Eds., Wiley-VCH:New York, Volume 12, **1998**, pp.327-365.
24. (a) Van Eijck, B.P., Mooij, W.T.M., Kroon, J., Acta Cryst., **1995**, B51, 99; (b) Van Eijck, B.P., Kroon, J. J. Comput. Chem., **1999**, 103, 9872.
25. Perlstein, J., J. Am.Chem. Soc., **1994**, 116, 11420.
26. Roberts, K. J.; Sherwood, J. N.; Yoon, C. S.; Docherty, R.: Chem. Mater. **1994**, 6, 658; Chen et. al. Phys. Chem. **1994**, 98, 5138.
27. Chaka, A.M., Zaniwski, R., Youngs, W., Tessier, C. & Klopman, G.: Acta Cryst., **1996**, B52, 165.
28. Gibson, K.D., Scheraga, H.A.: J.Phys.Chem., **1995**, 99, 3752.
29. Williams, D.E.: Acta Cryst., **1996**, A52(2), 326.
30. Gale, J.D.: Phil. Mag. B, **1996**, 73, 3;  
<http://argon.ch.ic.ac.uk/gale/Research/gulp.html>
31. Haugk, M.; Elsner, J.; Heine, Th.; Frauenheim, Th.; Seifert, G.: Comput. Mater.

Sci., **1999**, 13(4), 239.

<sup>32</sup>. Tan, A.; Harris, S.: Inorg. Chem., **1998**, 37, 2205.

<sup>33</sup>. Landrum, G.A.: Yet Another extended Hückel Molecular Orbital Package;  
<http://overlap.chem.cornell.edu:8080/yaehmop.html>

<sup>34</sup>. Themans, B.; Andre, J.M.; Bredas, J.L.: Mol.Cryst. Liq. Cryst., **1985**, 118;  
<http://www.chimie.fundp.ac.be/cta/docs/veh.html>

<sup>35</sup>. Ordejon, P.: Comput. Mater. Sci. **1998**, 12(3), 157.

<sup>36</sup>. Frauenheim, T.; Seifert, G.; Elstner, M.; Hajnal, Z.; Jungnickel, G.; Porezag, D.; Suhai, S.; Scholz, R.: Phys. Status Solidi B., **2000**, 217(1), 41.

<sup>37</sup>. Dewar, M.J.S.; Stewart, J.J.P. Chem. Phys. Lett., **1984**, 111, 416;  
<http://www.ccl.net/cca/software/NT/mopac6/index.shtml>

<sup>38</sup>. Kim, K.; Jordan, K. D.; J. Phys. Chem., **1994**, 98, 10089.

<sup>39</sup>. Simon, S.; Duran, M.; Dannenberg, J. J., J. Phys. Chem. A, **1999**, 103, 1640.

<sup>40</sup>. Guo, H.; Sirois, S.; Proynov, E. I.; Salahub, D. R., in Theoretical Treatments of Hydrogen Bonding, Had i, D., Editor, **1997**, Wiley, 49.

<sup>41</sup>. (a) Kohn, W.; Meir, Y.; Makarov, D. E., Phys. Rev. Lett., **1998**, 80, 4153; (b) Dobson, J. F.; Dinte, B. P. Phys. Rev. Lett., **1996**, 76, 1780; (c) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I., Phys. Rev. Lett., **1996**, 76, 102.

<sup>42</sup>. Becke, A. D., J. Chem. Phys., **1993**, 98, 5648.

<sup>43</sup>. Perdew, J. P.; Wang, Y., Phys. Rev., **1992**, B 45, 13244.

<sup>44</sup>. Lee, C.; Yang, W.; Parr, R. G., Phys. Rev. B, **1988**, 37, 785.

<sup>45</sup>. Ikeda, T.; Sprik, M.; Terakura, K.; Parrinello, M.: J. Chem. Phys., **1999**, 111(4), 1595.

<sup>46</sup>. Car, R.; Parrinello, M.: Phys. Rev. Lett. **1985**, 55, 2471;  
<http://parrserv2.mpi-stuttgart.mpg.de>;  
<http://pages.nyu.edu/~mt33/abstracts/manual/manual.html>

- <sup>47</sup>. Kresse, G.; Furthmüller, J.: Comput. Mat. Sci. **1996**, 6, 15;  
<http://tph.tuwien.ac.at/~vasp/>
- <sup>48</sup>. Blöchl, P.E.: Phys. Rev. B **1994**, 50, 17953; <http://www.zurich.ibm.com/~blo/>
- <sup>49</sup>. Bockstedte, M.; Kley, A.; Neugebauer, J.; Scheffler, M.: Comp. Phys. Commun. **1997**, 107, 187; <http://www.fhi-berlin.mpg.de/th/fhimd/>
- <sup>50</sup>. Payne, M.C.; et. al., Rev. Mod. Phys. **1992**, 64, 1045;  
<http://www.tcm.phy.cam.ac.uk/castep/>
- <sup>51</sup>. Kurth, S.; Perdew, J.P.; Blaha, P.: Int.J.Quant.Chem. **1999**, 75, 889;  
<http://info.tuwien.ac.at/theochem/wien97/>
- <sup>52</sup>. Guerra, C. F.; Snijders, J.G.; te Velde, G.; Baerends, E.J.: Theor. Chem. Acc. **1998**, 99, 391; <http://www.scm.com>
- <sup>53</sup>. DMol User Guide, San Diego:MSI, **1995**;  
<http://www.msi.com/materials/cerius2/dmol3.html>
- <sup>54</sup>. Andre, J.M.; Mosley, D.H.; Champagne, B.; Delhalle, J.; Fripiat, J.G.; Bredas, J.L.; Vanderveken, D.J.; Vercauteren, D.P.: in "METECC-94 Methods and Techniques in Computational Chemistry", E. Clementi Editor, Vol. B, Chapter 10, pp 423, STEF (Cagliari) (1993); <http://www.chimie.fundp.ac.be/cta/docs/plh-93.html>
- <sup>55</sup>. Jaffe, J.E.; Hess, A.C.: J. Chem. Phys. **1996**, 105, 10 983; Anchell, C. *et al.*, "NWChem, A computational chemistry package for parallel computers, Version 3.2.1," Pacific Northwest National Laboratory, Richland, Washington 99352-0999, **1998**.
- <sup>56</sup>. Pisani, C.: J. Mol. Struc. (THEOCHEM) **1999**, 463, 125; Dovesi, R.; Saunders, R.; Roetti, C.; Causà, M.; Harrison, N.M.; Orlando, R.; Apra, E.: CRYSTAL95 User's manual, Univerity of Torino, Torino, **1996**;  
<http://www.ch.unito.it/ifm/teorica/crystal.html>
- <sup>57</sup>. Pisani, C. Dovesi, R.; Roetti, C, Hartree-Fock ab-initio treatment of crystalline systems, Lecture Notes in Chemistry, Vol. 48, Springer Verlag, Heidelberg, **1988**.
- <sup>58</sup>. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahan, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.;



Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C.Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andre, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Deefres, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94: Gaussian, Inc., Pittsburgh, PA, **1995**.

<sup>59</sup>. Ojamäe, L.; Hermansson, K.; Dovesi, R.; Roetti, C.; Saunders, V. R., J. Chem. Phys., **1994**, 100, 2128.

<sup>60</sup>. (a) Towler, M. D.; »Hartree-Fock Theory of the Electronic Structure of Solids,= CRYSTAL Network School, September, **1995**; (b) <http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html>

<sup>61</sup>. (a) Schwenke, D. W.; Truhlar, D. G., J. Chem. Phys., **1984**, 82, 2418; (b) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F. III, J. Chem. Phys., **1986**, 2279; (c) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J., J. Chem. Phys., **1988**, 89, 3662; (d) Gutowski, M.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B., J. Chem. Phys., **1993**, 98, 4728; (e) Cook, D. B.; Sordo, J. A.; Sordo, T. L., Int. J. Quant. Chem., **1993**, 48, 375; (f) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H., Chem. Rev. **94** (1994) 1873.

<sup>62</sup>. (a) Boys, S. F.; Bernardi, F.: Mol. Phys., **1970**, 19, 553; (b) Meunier, A.; Levy, B.; Berthier, G.: Theor. Chim. Acta, **1973**, 29, 49; (c) Jansen, H.B.; Ross, P.: Chem. Phys. Lett., **1969**, 3, 40.

<sup>63</sup>. Mayer, I.; Surjan, P. R., Chem. Phys. Lett., **1992**, 191, 497; Turi, L.; Dannenberg, J. J.: J. Phys. Chem., **1993**, 97, 2488.

<sup>64</sup>. Turi, L.; Dannenberg, J. J.: J. Phys. Chem. **1993**, 97(11), 2488.

<sup>65</sup>. Simon, S.; Duran, M.; Dannenberg, J.J.: J. Chem. Phys., **1996**, 105, 11024; <http://stark.udg.es/~perico/bbopt.html>

<sup>66</sup>. Gianinetti, E.; Raimondi, M.; Tornaghi, E.: Int. J. Quantum Chem., **1996**, 60, 157; Gianinetti, E.; Vandoni, I.; Famulari, A.; Raimondi, M.: Adv. Quantum Chem., **1998**, 31, 251; Famulari, A.; Raimondi, M.; Sironi, M.; Gianinetti, E.: Chem. Phys. **1998**, 232(3), 275.

<sup>67</sup>. M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.J.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.Su, T.L.Windus, M.Dupuis, J.A.Montgomery J.Comput.Chem. **1993**, 14, 1347; <http://www.msg.ameslab.gov/GAMESS/GAMESS.html>

- <sup>68</sup>. Kitaura, K.; Morokuma, K.: Int.J.Quantum Chem. **1976**, 10, 325; Kitaura, K.; Morokuma, K.: in "Chemical Applications of Electrostatic Potentials", P.Politzer,D.G.Truhlar, Eds.Plenum Press, NY, 1981, p. 215; Cammi, R.; Bonaccorsi, R.; Tomasi J.:Theoret.Chim.Acta **1985**, 68, 271; Stevens, W.J.; Fink, W.H.: Chem.Phys.Lett., **1987**, 139, 15; Chen,W.; Gordon; M.S.: J.Phys.Chem. **1996**, 100, 14316.
- <sup>69</sup>. Raimondi. M.; Famulari, A.; Gianinetti, E.: Int. J. Quantum. Chem., **1999**, 74(2), 11024.
- <sup>70</sup>. (a) Halász, G.; Vibók, Á.; Valiron, P.; Mayer, I.: J. Phys. Chem., **1996**, 100(15), 6332; (b) Mayer, I. Int. J. Quantum. Chem. **1983**, 23, 341.
- <sup>71</sup>. Kieninger, M.; Suhai, S.; Mayer, I. Chem. Phys. Lett. **1994**, 230, 485.
- <sup>72</sup>. Schütz, M., Rauhut, G.; Werner, H.-J.: J. Phys. Chem. **1998**, 102, 5997; Runeberg, N.; Schütz, M.; Werner, H.-J. :J. Chem. Phys. **1999**, 110, 7210; <http://www.tc.bham.ac.uk/molpro/>
- <sup>73</sup>. Suhai, S., J. Chem. Phys. **1995**, 103(16), 7030.
- <sup>74</sup>. Suhai, S., J. Chem. Phys. **1994**, 101(11), 9766.
- <sup>75</sup>. Alfredsson,M.; Ojamae L.; Hermansson, K: Int. J. Quantum Chem., **1996**, 60(3), 767.
- <sup>76</sup>. Funk, K; Staemmler, V.; J. Chem. Phys., **1995**, 103(7), 2603.
- <sup>77</sup>. (a) Hirata, S., Iwata, S., J. Chem. Phys. **1998**; 109; 4147; (b) Hirata, S., Iwata, S., J.Phys.Chem. B; **1998**; 102(43); 8426.
- <sup>78</sup>. Jaffe, J.E.; Hess, A.C.: J. Chem. Phys., **1996**, 105(24), 10983.
- <sup>79</sup>. Saebo, S, Klewe, B., Samdal, S. Chem. Phys. Lett. **1983**, 97, 499.
- <sup>80</sup>. Sugano, S., Shulman, R. G., Phys. Rev., **1963**, 130, 517.
- <sup>81</sup>. Smit, P.H.; Derissen, J.L.; Van Duijneveldt, F.B. Mol. Phys., **1979**, 37(2), 501.
- <sup>82</sup>. (a) Rousseau, B.; Alsenoy, C. Van; Keuleers, R.; Desseyn, H. O.,J. Phys. Chem. **1998**, A.102(32), 6540; (b) Peeters, A.; Van Alsenoy, C.; Lenstra, A.T.H.; Geise, H.J.

J. Chem. Phys. **1995**, 103(15), 6608; (c) Van Alsenoy, C., Peeters, A., J. Mol. Struct. THEOCHEM, **1993**, 286, 125.

- <sup>83.</sup> Stefanovich, E. V., Truong, T. N., J. Phys. Chem. B, **1998**, 102(16), 3018.
- <sup>84.</sup> Xantheneas, S.S.: J. Chem. Phys., **1994**, 100(10), 7523.
- <sup>85.</sup> Suhai, S.: J. Phys. Chem., **1996**, 100, 3950.
- <sup>86.</sup> Cabaleiro-Lago, E.M.; Rios, M.A.: J. Chem. Phys., **1999**, 110(14), 6782.
- <sup>87.</sup> Nielsen, O.F.; Christiansen, D.H.; Rasmussen, O.H.: J. Mol. Struct., **1991**, 242, 273.
- <sup>88.</sup> King, B.F.; Weinhold, F.: J. Chem. Phys., **1995**, 103(1), 333.
- <sup>89.</sup> Stone, A.J.; Buckingham, A.D.: J. Chem. Phys., **1997**, 107(3), 1030.
- <sup>90.</sup> Cabaleiro-Lago, E.; Rios, M.: J. Chem. Phys., **1998**, 108(9), 3598.
- <sup>91.</sup> Karpfen, A.: J. Phys. Chem., **1996**, 100, 13474.
- <sup>92.</sup> Karpfen, A.: J. Phys. Chem., **1998**, 102, 9286.
- <sup>93.</sup> Masella, M.; Flament, J.P.: J. Chem. Phys., **1998**, 108(17), 7141.
- <sup>94.</sup> Chalaszinski, G.; Szczesniak, M.M.; Cieplak, P.; Scheiner, S.: J. Chem. Phys., **1991**, 94, 2873.
- <sup>95.</sup> Parra, R.D.; Zeng, X.C.: J. Chem. Phys., **1999**, 110(13), 6329.
- <sup>96.</sup> Gonzales, L.; Mo, O.; Yanez, M.: J. Chem. Phys., **1999**, 111(9), 3855.
- <sup>97.</sup> Sum, A.K.; Sandler, I.S.: J. Phys. Chem. A, **2000**, 104(6), 1121.
- <sup>98.</sup> Cabaleiro-Lago, E.M.; Rios, M.A.: J. Chem. Phys., **2000**, 112(5), 2155.
- <sup>99.</sup> Ludwig, R.; Weinhold, F.; Farrar, T. C.: J. Chem. Phys., **1997**, 107(2), 499.
- <sup>100.</sup> Grigorenko, B.L.; Moskovsky, A.A.; Nemukhin, A.V.: J. Chem. Phys.; **1999**; 101(10); 4442.
- <sup>101.</sup> (a) Strout, D.L.; Scuseria, G.E., J. Chem. Phys., **1995**, 102, 8448 ; (b)

[http://www.chem.joensuu.fi/people/juha\\_muilu/Research/ab\\_initio\\_method.html](http://www.chem.joensuu.fi/people/juha_muilu/Research/ab_initio_method.html)

- <sup>102.</sup> (a) Turi, L.; Dannenberg, J. J. J. Phys. Chem. **1993**, 97, 12197; (b) Turi, L.; Dannenberg, J. J. J. Am. Chem. Soc. **1994**, 116, 8714.
- <sup>103.</sup> (a) Turi, L.; Dannenberg, J. J. Chem. Mater. **1994**, 6, 1313; (b) Turi, L.; Dannenberg, J. J. J. Phys. Chem. **1992**, 96, 5819.
- <sup>104.</sup> (a) Turi, L., Dannenberg, J. J., J. Phys. Chem.; **1996**; 100 (23); 9638; (b) Vinson, L. K.; Dannenberg, J. J. J. Am. Chem. Soc. **1989**, 111, 2777.
- <sup>105.</sup> Halbout, J.M.; Tang, C.: In: Nonlinear Optical Properties of Organic Molecules and Crystals. Chemla, D.S.; Zyss, J. Eds. Acad. Press, NY 1987, vol. 1, p. 385; Mestechkin, M. M.: Optics Spectrosc., **1996**, 81(5), 714.
- <sup>106.</sup> (a) Tanaka, H.; Touhara, H.; Nakanishi, K.; Watanabe N.: J. Chem. Phys., **1984**, 80(10), 5170; (b) Tanaka, H.; Nakanishi, K.; Touhara, H.: J. Chem. Phys., **1985**, 82(11), 5184; (c) Astrand, P.O.; Wallqvist, A.; Karlstrom, G.; Linse, P.: J. Chem. Phys.; **1991**; 95(11); 8419; (d) Astrand, P.O.; Wallqvist, A.; Karlstrom, G.: J. Chem. Phys.; **1994**; 100(2) 1262; (e) Hernandez-Cobos, J.; Ortega-Blake, I.; Bonilla-Marin, M.: J. Chem. Phys.; **1993**; 99(11) 9122; (f) Boek, E.S.; Briels, W.J.; van Eerden, J.; Feil, D.: J. Chem. Phys.; **1992**; 96(9) 7010; (g) Boek, E.S.; Briels, W.J.: J. Chem. Phys.; **1993**; 98(2) 1422.
- <sup>107.</sup> Godínez, L.A.; Schwartz, L.; Criss, C.M.; Kaifer, A.E.: J. Phys. Chem. B, **1997**, 101(17), 3376; Shen, X.; Belletête, M.; Durocher, G.: J. Phys. Chem. B, **1997**, 101(41), 8212; Wallqvist, A.; Covell, D.G.; Thirumalai, D.: J. Am. Chem. Soc., **1998** 120(2), 427.
- <sup>108.</sup> Castronuovo, G.; Elia, V.; Postiglione, C.; Velleca, F.: Thermochim. Acta **1999**, 339(1), 11; Shelton, V.M.; Sosnick, T.R.; Pan, T.: Biochemistry **1999**, 38(51), 16831; Griko, Yu.V.; Kutysenko, V.P.: Biophys. J., **1994**, 67(1), 356.
- <sup>109.</sup> Swaminathan, S.; Craven, B.M.; McMullan, R.K.: Acta Cryst., **1984**, B, 40, 300.
- <sup>110.</sup> Kontoyianni, M.; Bowen, P., J. Comput. Chem., **1992**, 13, 657.
- <sup>111.</sup> Meier, R. J.; Coussens, B., J. Mol. Struct., **1992**, 253, 25.
- <sup>112.</sup> Gobbi, A.; Frenking, G., J. Am. Chem. Soc., **1993**, 115, 2362.

- <sup>113.</sup> Dixon, D. A.; Matsuzawa, N., J. Phys. Chem., **1994**, 98, 3967.
- <sup>114.</sup> King, S. T., Spectrochim. Acta, **1972**, 28, 165.
- <sup>115.</sup> Godfrey, P.D.; Brown, R.D.; Hunter A.N.; J. Mol. Struct., **1997**, 413-414, 405;  
Brown, R. D; Godfrey, D.; Storey, J., J. Molec. Spect., **1975**, 58, 445.
- <sup>116.</sup> Rousseau, B.; Van Alsenoy, C.; Keuleers, R.; Desseyn, H.O.: J. Phys. Chem., **1998**, A102, 6540.
- <sup>117.</sup> Langer, J.; Schrader, B.; Bastian, V.; Jacob, E, Fresenius J. Anal. Chem., **1995**, 352, 489.
- <sup>118.</sup> Hadzi, D.; Kidric, L.; Knezevic, Z.V.; Barlic, B.: Spectrochim. Acta, **1976**, A32, 693.
- <sup>119.</sup> Keuleers, R.; Desseyn, H. O.; Rousseau, B.; Van Alsenoy, C.,J. Phys. Chem., **1999**, A.103, 4621.
- <sup>120.</sup> Perez, J.; Dupuis, M.: J. Phys. Chem., **1991**, 95, 6526.
- <sup>121.</sup> Belosludov, R.V.; Li, Z.Q.; Kawazoe, Y. Molecular Engineering **1999**, 8, 105.
- <sup>122.</sup> Harris, K.D.M.; Hollingworth, M.D. Urea, thiourea, and selenourea inclusion compounds, in J.-M. Lehn (Ed.), Comprehensive Supramolecular Chemistry, Vol. 6, Elsevier Science Ltd., Oxford, **1996**, 177.
- <sup>123.</sup> Rutherford, J.S.; Calvo, C.: Z.Kristallogr., **1969**, 128, 229.
- <sup>124.</sup> Suzuki, K.; Onishi, S.; Koide, T.; Seki, S. Bull. Chem. Soc. Jap., **1956**, 29, 127.
- <sup>125.</sup> Kabo, G.Ya.; Miroshnichenko, E.A.; Frenkel, M.L.; Kozyro, A.A.; Simirskii, V.V.; Karsulin, A.P.; Vorob-eva, V.P.; Lebedev, Yu.A. Bull. Acad. Sci. USSR, Div. Chem. Sci. **1990**, 662.
- <sup>126.</sup> (a) Dovesi, R.; Causa, M., Orlando, R., Roetti, C.; Saunders, V. R., J. Chem. Phys., **1990**, 92, 7402; (b) Gatti, C.; Saunders, V. R.; Roetti, C. J. Chem. Phys., **1994**, 101, 10686.
- <sup>127.</sup> Miao, M.S.; Van Doren, V.E.; Van Alsenoy, C.; Martinis, J.L.: Proc. 5<sup>th</sup> Electronic Conf. On Comput. Chem. 1997;  
<http://hackberry.chem.niu.edu/ECCC5/articles/article31/urea.html>

- <sup>128.</sup> Gilkerson, W.; Srivastava, K., J. Phys. Chem., **1960**, 64, 1485.
- <sup>129.</sup> Lefebvre, J. Solid State Commun., **1973**, 13, 1873.
- <sup>130.</sup> Lefebvre, J.; Fontaine, H.; Fouret, R.: J. Raman Spectrosc. **1975**, 4(2), 173.
- <sup>131.</sup> Spackman, M.A.; Byrom, P.G.; Alfredsson, M.; Hermansson, K. Acta Cryst., **1988**, A55, 30.
- <sup>132.</sup> (a) Mullen, D., Hellner, E. Acta Cryst., **1978**, B34, 1624. (b) Swaminathan, S., Craven, B. M., Spackman, M. A.; Stewart, R. F. Acta Cryst., **1984**, B40, 398; (c) Zavodnik, V., Stash, A., Tsirelson, V., Vries, R. de, Feil, D. Acta Cryst., **1999** B55, 45.
- <sup>133.</sup> (a) Spackman, M.A.; Weber, H.P.; Craven, B.M. J. Am. Chem. Soc., **1988**, 110, 775; (b) Suponitsky, K.Yu.; Tsirelson, V., Feil, D. Acta Cryst., **1999** B55, 45.
- <sup>134.</sup> Abramov, Y.A.; Volkov, A.; Guang Wu, G.; Coppens, P.: J. Phys. Chem. B; **2000**; 104(9); 2183.
- <sup>135.</sup> De Vries, R. Y., Feil, D.; Tsirelson, V. G.: Acta Cryst., **2000**, B56, 118.
- <sup>136.</sup> Volkov, A., Wu, G.; Coppens, P.: J. Synchrotron Rad., **1999**, 6, 1007.
- <sup>137.</sup> Kutoglu, A., Scheringer, C., Meyer, H., Schweig, A. Acta Cryst. **1983**, B38, 2626; Mullen, D. Acta Cryst. **1983**, B38, 2620; Gao, Y., Coppens, P. Acta Cryst. **1989**, B45, 298.
- <sup>138.</sup> Takahashi, I.; Onodera, A.; Shiozaki, Y.: Acta Cryst., **1990**, B 46, 661.
- <sup>139.</sup> Ashcroft, S.J. J. Chem. Soc. A, **1970**, 1020.
- <sup>140.</sup> Gomez, T.; Alfonso, L.; Sabbah, R. Thermochim. Acta **1982**, 57, 67.